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RESEARCH OF THE PROPERTIES OF HETEROGENEOUS CATALYSTS OF ACETONITRILE SYNTHESIS

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ABSTRACT

This article discusses the study of the properties of heterogeneous catalysts for the synthesis of acetonitrile. The process of condensation of acetylene with ammonia in the presence of catalysts based on cadmium fluoride (CFA-1, CCFA-1, CFA-2, CZA-1) has been studied. The condensation of acetylene with ammonia has been studied in the presence of cadmium fluoroaluminum catalysts . It was found that CFA after the first cycle of operation is stabilized and the yield of acetonitrile decreases to a minimum and ranges from 5.0 to 10.0%. The main reaction products are mixtures of pyridine bases, among which 2- and 4-methylpyridines predominate.

It was found that as the catalyst is used, its activity gradually decreases. The entrainment of metallic cadmium from the catalyst is observed.

Introduction. The widespread industrial use of acetonitrile is delayed due to acetonitrile from more accessible compounds and the selection of active catalysts, the lack of cheap and convenient methods for its preparation. Therefore, the creation of new methods of synthesis with higher selectivity and productivity is an urgent task [1,2]. Acetonitrile is a universal solvent for many organic and inorganic salts, oils, resins, nitrocellulose, esters, acids, celluloid, alkalloids, polymers, and other compounds. It is used in the production of amines, acid amides and pesticides, it is also used as a component of azeotropic distillation, selective extraction and as a solvent in many processes.

The first syntheses of acetonitrile and pyridine bases from acetylene and ammonia are given in the works of well-known chemists Meyer, Ramsay and Dewar [3-5] who, passing a mixture of acetylene with ammonia or hydrocyanic acid without a catalyst into a hot tube, obtained acetonitrile, a mixture of nitrogen-containing bases, etc.

The study of the condensation reaction of acetylene with ammonia was carried out at the beginning of the 20th century by the famous Russian organic chemists A.E. Chichibabin and P.A. Moshkin who, passing a mixture of acetylene with ammonia over catalysts containing oxides of aluminum, chromium, iron, isolated acetonitrile, a mixture of pyridine bases, ethylamines, resin, etc. [6, 7].

Japanese researchers [8] studied the condensation of acetylene with ammonia in the presence of alumina promoted with alkali metal salts and found that this catalyst has sufficient selectivity for the formation of acetonitrile. They studied in detail the influence of various factors on the course of the process. Based on the data obtained, it was found that the rate-limiting stage of the reaction is the formation of acetonitrile during the interaction of adsorptive acetylene with ammonia on areas of the catalyst surface that do not have acidic properties. Side reactions - the formation of hydrocyanic acid, as well as the decomposition of acetylene and ammonia, occur on the non-acidic surface of the catalyst. At the same time, the reaction of polymerization and the formation of pyridine bases occurs on the acidic surface.

According to other authors [9], the catalyst has two types of acid sites: the first forms acetonitrile, the second forms pyridine bases, resins, and other by-products.

By the condensation of acetylene with ammonia in the liquid phase, Reppe [10] obtained 2-methyl-5-ethylpyridine in 75% yield with a small amount of by-products, acetonitrile and etc.

It was found that chlorides of alkali metals do not accelerate the reaction of formation of acetonitrile, but suppress side reactions and, therefore, increases the yield of acetonitrile.

American scientists [11] condensed acetylene with ammonia at 440-550°C in the presence of molten zinc chloride to obtain acetonitrile in 60% yield. Various systems of molten metal chlorides were used as the synthesis of acetonitrile. The most active was the system containing molten zinc chloride. The authors found that an increase in the ratio of acetylene: ammonia from 1:1 to 7:1 leads to a decrease in the yield of acetonitrile due to side reactions.

The synthesis of acetonitrile from acetylene and ammonia has been studied in the presence of a heterogeneous catalyst .

Acetonitrile as a starting material in various syntheses can be obtained in several ways [2]:

a) in industry, acetonitrile is obtained by ammonolysis of acetic acid at 300 - 400 ° C using a small excess of ammonia;

b) in the laboratory, acetonitrile is obtained by dehydration of acetamide under the action of P_2O_5.

At present, in Uzbekistan, the most promising industrially, is the synthesis of acetonitrile from acetylene and ammonia.

The selection of selective, high-performance catalysts and process conditions can be achieved with a high yield of acetonitrile from an important product of the main organic synthesis product [12 - 16].

Materials and methods. As noted above, zinc oxide catalyzes the formation of acetonitrile from acetylene and ammonia. In order to obtain comparative data, a number of catalysts were prepared, [17] in which the zinc oxide content ranged from 3.0 to 20.0 wt, %. When studying the condensation of acetylene with ammonia in the presence of a zinc-aluminum catalyst (CA-1) containing zinc oxide in an amount of 20.0%, the formation of acetonitrile passes through a maximum (Fig. 1.) A further increase in the ZnO content in the catalyst leads to a decrease in its activity. When passing a mixture of acetylene with ammonia at a ratio of 1:2 vol., At a rate of 150 l/l•cat•h at temperatures of 400-420° C, acetonitrile was obtained with a yield of 58.0% of the theoretically possible. Zinc-aluminum catalyst TsA-1 operates in the temperature range of 380-450° C for 8 hours. After that, he significantly loses his activity. The conversion of acetylene in the presence of this catalyst does not exceed 70%. Carrying out the process at relatively elevated temperatures (450° C and above) leads to a decrease in the selectivity of the catalyst. If at temperatures of 380-420° C condensate is formed, consisting mainly of acetonitrile, then with an increase in temperature, mixtures of nitrogen-containing heterocycles appear in the catalyst, since 2-methylpyridine, 4-dimethylpyridines and etc.

Results and their discussion. Based on preliminary studies, we came to the conclusion that zinc oxide on alumina does not meet the requirements for industrial catalysts in the synthesis of acetonitrile.

Further studies on the synthesis of acetonitrile from acetylene and ammonia were carried out in the presence of a chromium-aluminum catalyst (XA-I). The study of this catalyst was carried out in the temperature range of 280-480° C.

Chromium-aluminum catalysts are widely used in industry and their use in the reaction of synthesis of acetonitrile is of undoubted interest. It is known that catalysts based on chromium oxide are used in dehydrogenation reactions. The reaction of formation of acetonyrile from acetylene and ammonia also belongs to the dehydrogenation processes, therefore we used chromium oxide as a contact in this reaction.

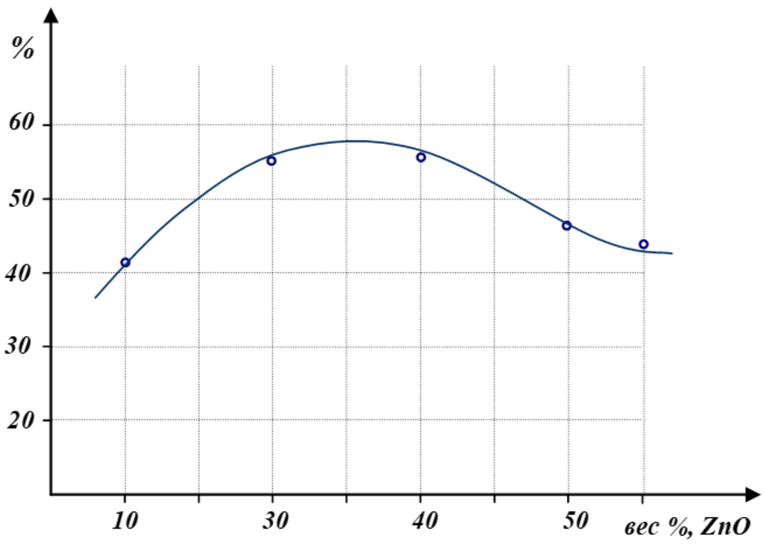

Fig. 1. Dependence of the CH_3CN yield on the ZnO content in the catalyst.

In the course of the study, the effect of temperature, volume ratio of ammonia to acetylene, space velocity, etc., was studied on the yield of acetonitrile . The analysis showed that in the presence of a chromium-alumina catalyst, acetonitrile is mainly formed from acetylene and ammonia. In this case, the process temperature is reduced to 60-140° C in comparison with known catalysts, for example, zinc oxide or aluminum oxide. The catalyst, without reducing its initial activity, works for 18 hours, after which it needs to be regenerated.

The effect of temperature was studied in the range of 300-420° C (Fig. 2.). As can be seen from the data in Fig. 2, an increase in temperature to 360 ° C promotes the formation of acetonitrile. A further increase in temperature leads to a decrease in the yield of acetonitrile due to by-products (the formation of methylpyridines, decomposition of acetylene, etc.).

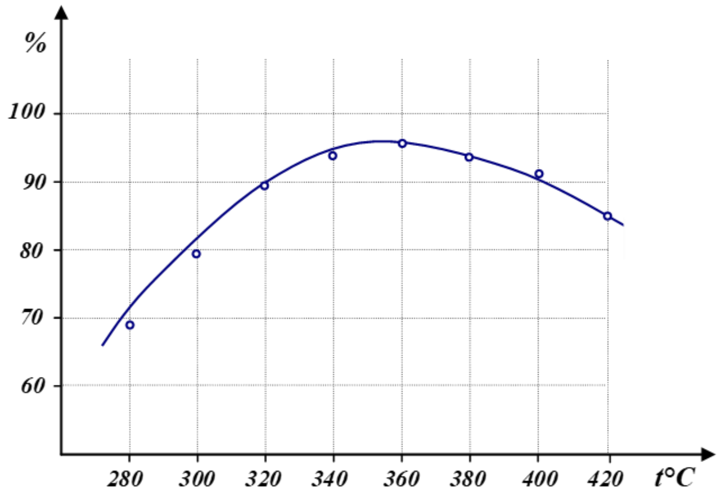

Fig. 2. Dependence of the yield of acetonitrile on temperature (in %, for passed acetylene)

The process of condensation of acetylene with ammonia has been studied in the presence of catalysts based on cadmium fluoride (CFA-1, CCFA-1, CFA-2, CZA-1). The condensation of acetylene with ammonia has been studied in the presence of cadmium-fluoroaluminum catalysts . The reaction was carried out in the temperature range 270-360° C, with the ratio of acetylene and ammonia 1:2.

Table 1: Key performance indicators of the CFA-1 catalyst

№	Time from the beginning of the experiment, hour	Temperature,°C	Conversion acetylene %	Composition of liquid products,% mass			
				Acetonitrile	2-methylpyridine	4-methylpyridine	Higher pyridines
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1.	8	260	42,0	72,0	15,0	8,0	3,0
2.	16	270	54,0	66,0	18,0	10,0	5,0
3.	26	280	65,0	53,0	26,0	14,0	6,0
4.	43	292	74,0	52,0	34,0	12,0	1,0
5.	48	304	78,0	46,0	36,0	13,0	3,0
6.	60	310	83,0	56,0	26,0	14,0	2,0
7.	72	320	84,0	54,0	28,0	13,0	4,0
8.	86	360	86,0	48,0	34,0	12,0	5,0

In purpose of determining the work resource of the catalyst and establishing the main parameters of the process, a series of experiments were performed on one catalyst sample (CFA - 1). The experiments were carried out on a laboratory setup in a stainless steel reactor with 100 cm^3 of the bulk volume of the catalyst with a total volumetric rate of 180-200 L / L•cat•h (Table 1).

As can be seen from the data in the table, the conversion of acetylene at 260-280°C is 42-65%. With increasing temperature, the conversion of acetylene reaches 86%. Selectivity of the formation of acetonitrile with the expiration of the increase in selectivity during the formation of 2- and 4-methylpyridines.

It was found that the CFA catalyst stabilizes after the first cycle of operation, and the yield of acetonitrile decreases to a minimum and ranges from 5.0 to 10.0%.

The main reaction products are the mixtures of pyridine bases, among which 2- and 4-methylpyridines predominate.

Experimental data show that acetonitrile can be successfully synthesized in the presence of CCA catalysts. The use of zinc-chromium or cadmium-fluorine-aluminum catalysts in the synthesis of acetonitrile does not provide high conversion, selectivity, and other parameters of the process.

In the experiments, cadmium sulfate was used as a catalyst in the synthesis of acetonitrile. Of cadmium compounds, cadmium sulfate is readily available and catalysts based on it are prepared in the usual way.

To select the optimal content of the active component (cadmium sulfate), which has the highest activity in the reactions of synthesis of acetonitrile, a series of preliminary experiments were carried out with various samples differing in the content of cadmium sulfate. All experiments with a cadmium sulfate catalyst on alumina were carried out at the temperatures of 300 - 400° C, the volumetric velocities of the gas mixtures of 350 L / L•cat•h, catalysts volume 100 cm^3, and a constant ratio of acetylene and ammonia is 1:2.5 vol.

It was found that with an increase in the content of cadmium sulfate in the catalyst to 30% by weight, the yield of acetonitrile passes through a maximum (corresponding to a cadmium sulfate content of 20% by weight). A further increase in the content of cadmium sulfate in the catalyst leads to a decrease in activity. Apparently, the observed maximum of activity corresponds to the coverage of the surface by a monolayer.

X-ray diffraction patterns were taken of catalysts with a cadmium sulfate content of 5.0 to 30% by weight. In X-ray diffraction patterns, characteristic lines for cadmium sulfate were not found for catalysts, containing up to 20% by weight of cadmium sulfate. In samples containing 20-30% cadmium sulfate, clear lines appear, characteristic of cadmium sulfate crystals.

Differmograms of the cadmium sulfate catalyst were recorded to a temperature of 700° C. It was found that, heating the catalyst to 700° C leads to phase changes. The cadmium sulfate catalyst obtained by calcining at 700° C, exhibits an activity nearly two times lower than that of catalysts obtained by calcining at 450° C.

Further studies were carried out on a catalyst containing 20% cadmium sulfate calcined at 450 - 500° C.

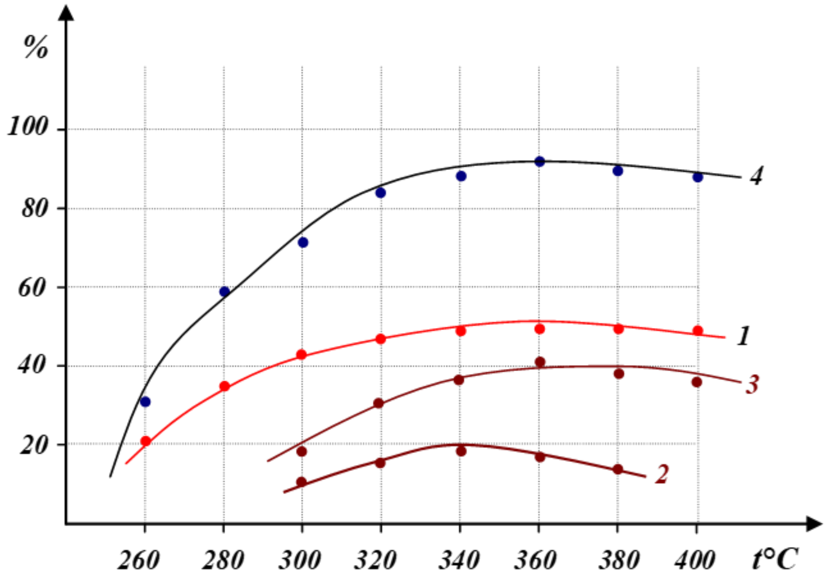

Fig. 3. Dependence of the yield of acetonitrile on temperature
1- acetonitrile; 2- 2-methylpyridine; 3- 4-methylpyridine; 4- conversion of acetylene.

The influence of temperature, space velocity, ratio, operating time and other factors were studied on the yield of acetonitrile and the selectivity of the process [18].

The effect of temperature was studied in the temperature range 260 - 400° C.

As can be seen from Fig. 3, with an increase in temperature from 260 to 360°C, an increase observed in the yield of acetonitrile, as well as 2- and 4-methylpyridines.At 360° C, the yield of 2- and 4-methylpyridines reaches a maximum of 10.0%, respectively. The conversion of acetylene at 350° C is achieved up to 90%.

Table 2 shows the changes in the activity of the cadmium sulfate catalyst with time at a temperature of -340° C, a ratio of acetylene and ammonia of 1:3, and a volumetric velocity of acetylene of 75 l / l•cat•h.

Table 2

Change in the activity of cadmium sulfate catalyst over time

№	Time from the beginning of the experiment, hour	Acetylene conversion,%	Composition of liquid products, reactions,%		
			Acetonitrile	2-methylpyridine	4-methylpyridine
1	**2**	**3**	**4**	**5**	**6**
1.	4	98,0	82,0	10,0	4,0
2.	8	94,0	80,0	14,0	3,0
3.	12	90,0	72,0	18,0	7,0
4.	16	82,0	68,0	21,0	10,0
5.	20	72,0	60,0	25,0	13,0
6.	24	67,0	54,0	27,0	16,0
7.	28	60,0	48,0	22,0	11,0

As can be seen from the data table. 2, the activity of the cadmium sulfate catalyst with respect to acetonitrile decreases over time, which is directly related to the removal of active centers, especially cadmium, by the flow of starting reagents - acetylene and ammonia, which is evidenced by a decrease in the conversion of acetylene.

Conclusion.

Based on the studies carried out, it can be concluded that the reaction of acetylene with ammonia is complex. Regardless of the nature of the catalysts used, the reaction can be directed towards the formation of acetonitrile, or towards the formation of 2- and 4-methylpyridines. Among the studied zinc-chromium-cadmium-aluminum catalysts, promoted by sodium carbonate contact masses, have a sufficiently high activity, selectivity and stability, and they can be recommended for use on an industrial scale.

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